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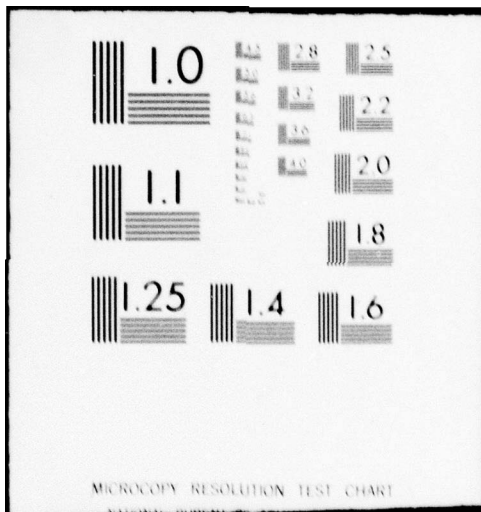
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**Advanced Ceramics and Composites for Underwater
Acoustic and Engineering Applications.**

R.C. Pohanka, R.W. Rice and P.L. Smith

Ceramics Branch
Material Science and Technology Division

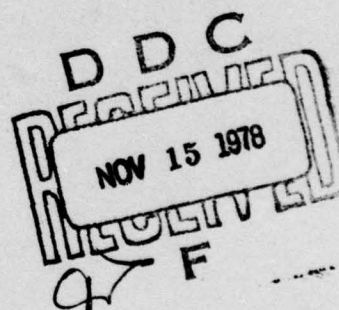
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mines and special high power applications is also a materials area with device application. Further, the development of highly anisotropic materials (SbSI) would allow for more sensitive and reliable designs of hydrophones. These materials could also be important in the development of flexible composites. Finally basic understanding of domain processes in ferroelectric glasses offers an opportunity to contribute a unique material that would allow the development of new optical, dielectric and piezoelectric devices.

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ADVANCED CERAMICS AND COMPOSITES FOR UNDERWATER ACOUSTIC AND ENGINEERING APPLICATIONS

INTRODUCTION

This report outlines new approaches to the development of piezoelectric and ferroelectric materials which could provide significant systems impact.

This impact can result both from significant improvements in existing devices and from making new types of devices feasible. Systems and devices which could benefit from this materials research are summarized in Table I. The list of Table I is not meant to be exhaustive since exploration of the concepts discussed here may well provide the impetus for other unforeseen and possibly more important opportunities for material development. It is probable that not all of the suggested approaches will work out as optimistically as might now be anticipated. It is felt, however, that some of the developments from the approaches discussed could be as important as the introduction of lead zirconate titanate (PZT) ceramics.

In addition to the applications listed in Table I, the need to develop an understanding of materials which permits production of materials whose tailored properties have specific transduction mechanisms is also important, and this materials research would contribute substantially in this fundamental area.

BACKGROUND

PZT type ceramics developed in the middle fifties have dominated the sonar field since 1969. Extensive efforts over the last twenty years in the U.S., Europe, Japan and U.S.S.R., have optimized most of properties of conventional PZT bodies. Thus benefits from continued research on such conventional PZT materials would be largely economic and one should not expect significant further improvement in properties.

Note: Manuscript submitted August 11, 1978.

Table I

<u>Material Development</u>	<u>Applications (Anticipated)</u>
Ceramic - Polymer Composites	Conformal Arrays Thin Line Towed Arrays New Hydrostatic Sensors Piezoelectric Torpedo Fusing Devices
Ceramic - Ceramic Composites	Small, Compact, Light Weight Active Transducers High Power Special Applications More Reliable Standard Systems
Electrostrictive Materials	Special High Power Applications Tuneable Arrays
New Compounds, e.g. SbSI	Sensitive Reliable Hydrostatic Hydrophones
Ferroelectric Glasses	Optical Hydrophones

New opportunities for development of materials beyond conventional PZT materials are seen in composite materials, new compounds and new modes of operation as summarized in Table I. These opportunities result from combination of new concepts and materials integrated with known and/or developing concepts. While many of the materials developments could have impact on existing systems some are such that new systems could be developed, e.g. optical hydrophones.

OPPORTUNITIES FOR DEVELOPMENT OF NEW MATERIALS

A. Flexible Ceramic-Organic Composites

The development of ceramic-organic composites which combine the flexibility of a polymer with tailored piezoelectric and dielectric properties of a ceramic could have major impacts on passive systems such as thin line towed and hull mounted conformal arrays. These flexible composites could also provide a promising material for active flexible piezoelectric devices. Limited early efforts by Gould showed that a flexible piezoelectric body can be made by embedding piezoelectric ceramic particles in a polymer matrix. The most promising composite material produced by this approach, however, was at Honeywell.¹ This new material had a voltage response larger than the best piezoelectric polymer, polyvinylidene fluoride (PVF₂), but below the response needed for practical applications.

These past composites were limited because of the lack of dielectric connectivity of the piezoelectric particles. This lack of connectivity results in very small electric fields over the active ceramic which in turn results in low permittivity and incomplete poling; thus low piezoelectric response. Two key developments show potential for providing polymer-ceramic composites to reach useful levels of properties and open possibilities for new applications. First, analysis shows that with high dielectric connectivity (parallel model, Appendix A) and lack of mechanical interaction between piezoelectric particles that large piezoelectric voltage coefficients (g) and tailored permittivity are possible. Mechanical interaction between piezoelectric particles is minimized by use of a low stiffness polymer that is also required for flexibility. Further this analysis shows that if the sound pressure can be concentrated onto the ceramic phase of the composite a maximum voltage response can be obtained.

The second major development is the recognition that the dielectric connectivity and mechanical flux concentration can be readily achieved in a ceramic polymer composite. Thin,

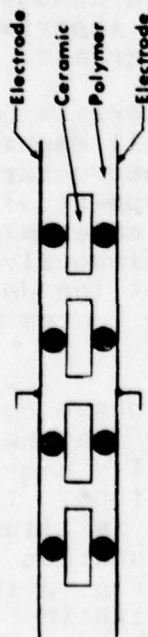
0.05 mm, disks of PZT materials for filter applications are mass produced; fully polarized and electroded. Combining these PZT disks into a polymer allows for the construction of a flexible fully polarized and oriented composite. Preliminary work at NRL, Fig. 1, has shown that flexibility can be achieved with 3-3 voltage responses five times that of PVF₂ and 3-3 charge response thirty times PVF₂ which is the current leading candidate for flexible piezoelectric applications. These results give a possible figure at merit for hydrophone applications 150 times that of PVF₂. While these composites are a major improvement over PVF₂ additional work is needed. For example hydrophone applications, involving long cables, require dielectric constants ten times the present composite with similar voltage response so that preamplifiers are not needed. Development of high permittivity materials or use of new compounds such as SbSI discussed later should make such development feasible. Also further improvement in preamplifier technology may reduce the permittivity requirements. For conformal and towed arrays hydrostatic loading could reduce the response and thus further improvement in both hydrostatic voltage and charge responses may be necessary.

Each individual piezoelectric element or group of elements in the above composites Fig. 1 could be made individually addressable, e.g. using thick film technology. This would allow for the possibility of active flexible materials with shaped or formed acoustic beams. These materials could find application as conformal fusing devices.

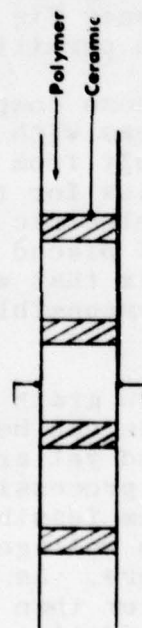
Further improvements of flexible composites should be possible by investigating several areas. One of the most important is to obtain experimental and analytical understanding of the effects of the size, shape and spacing of the ceramic phase in the polymer on the electroelastic properties of the composite. This understanding will allow for the maximum voltage response from the material for specific loading conditions such as hydrostatic loading while maintaining flexibility. Further, the spacing will be important to tailoring the dielectric response of the composite. More detailed evaluation of piezoelectric polymers as the flexible phase as well as effects of interfacial charge in the composite, both of which could enhance sensitivity, should also be carried out. In conclusion the study of the relationship of the piezoelectric and mechanical properties to structure in flexible composite materials offers the possibility to develop new materials and devices for underwater acoustic applications.

B. High Permittivity Ceramic-Ceramic Composites

The development of stable ceramic composites with high



Actual Volumes of Ceramic and Polymer



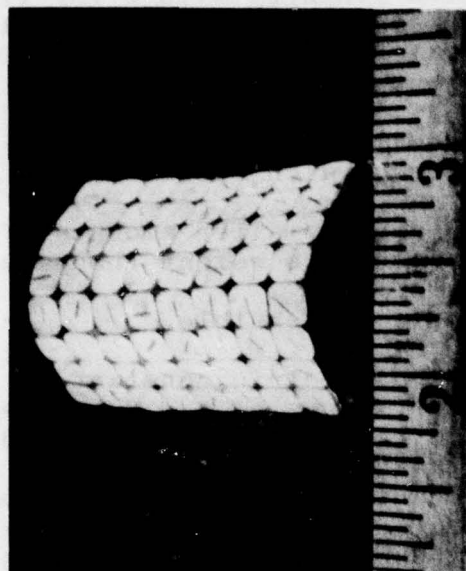
Effective Dielectric Volumes
of Ceramic and Polymer

PROPERTIES

PZT	PVF ₂	NRL Flexible Composite
$\epsilon_{33} = 1300$	$\epsilon_{33} = 14$	$\epsilon_{33} \approx 25 - 50$
$d_{33} = 200 \times 10^{-12} \text{ C/N}$	$d_{33} = 14 \times 10^{-12} \text{ C/N}$	$d_{33} = 180 \times 10^{-12} \text{ C/N}$
$g_{33} = 26 \times 10^{-3} \frac{\text{V-m}}{\text{N}}$	$g_{33} = 160 \times 10^{-3} \frac{\text{V-m}}{\text{N}}$	$g_{33} = 750 \times 10^{-3} \frac{\text{V-m}}{\text{N}}$

* Can be tailored via structure; ** g_{33} variable depending on ϵ_{33} .

Fig. 1. Flexible composites; showing one method for tailoring dielectric properties and comparisons of the properties of composites to PZT and PVF₂.



permittivity ($\epsilon \geq 5000$) and maintaining piezoelectric coupling at present levels (~ 0.6) would have important systems advantages. Since power output scales linearly with ϵ for fixed transducer size, and transducer size scales inversely with ϵ for fixed power output high ϵ materials could have the following systems impact.

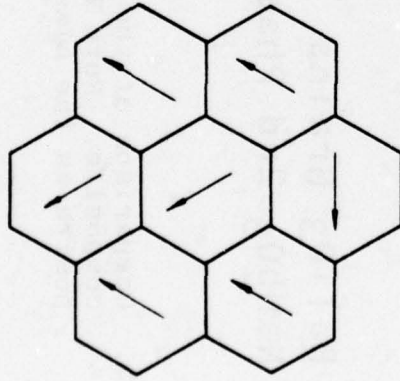
1. More reliable operation in existing systems because lower voltages could be used with equivalent power output.
2. Improved decoys and mines because smaller amounts of ceramic could be used to control the weight (bouyancy).
3. New, high power systems should be feasible.

A theoretical upper limit to dielectric constant of piezoelectric materials is not known. Values of $\epsilon \sim 20,000$ are observed and materials with 5-7000 can be readily prepared. However, practical sonar materials have been limited to ~ 1200 because of non linearities, mechanical and electrical losses experienced with past high ϵ materials. Such non-linear and lossy behavior is fundamentally due to domain nucleation and domain wall motion. Charge and internal stresses at grain boundaries are critical to the domain motion responsible for the nonlinearities. Grain boundary phases are possible ways of modifying both boundary charges and stresses so that high permittivity materials could be successfully used in sonar devices. Thus the development of new piezoelectric composites using selected grain boundary phases Fig. 2 offers important new opportunities to develop high permittivity materials.

The initial development of these composite materials could be carried out in a number of areas with the overall emphasis on using mechanisms that can result from new microstructures (.e.g. the grain boundary) to allow for the development of new properties. For example high dielectric constant materials could be used as a grain phase if placed in a continuously connected antiferroelectric matrix that would limit the domain formation and wall motion responsible for the losses and nonlinearities.

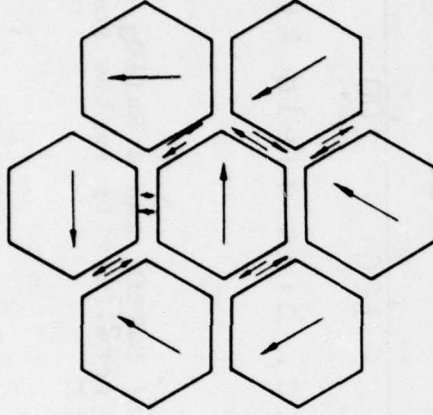
A key factor in designing such grain boundary phase composites is whether boundary phases can be selected that have the desired electrical effects and yet are chemically compatible with the grain phase and processing conditions. It is felt that such compatibility is feasible. This is illustrated by the development of high voltage, low saturation commercial $\text{BaTiO}_3\text{-NaNbO}_3$ capacitors. As shown in Fig. 3 the permittivity of BaTiO_3 drops faster than desired with increasing voltage. However, the addition of a few % of NaNbO_3

Current Materials $\text{Pb}(\text{Zr Ti})\text{O}_3$



1. PZT grains are shown schematically as hexagons directly bonded to one another.
2. The permittivity (ϵ) is limited to ~ 1200 .
3. The stresses between grains are the major driving force for instability.
4. Piezoelectric coupling $K_{33} \sim 0.7$.

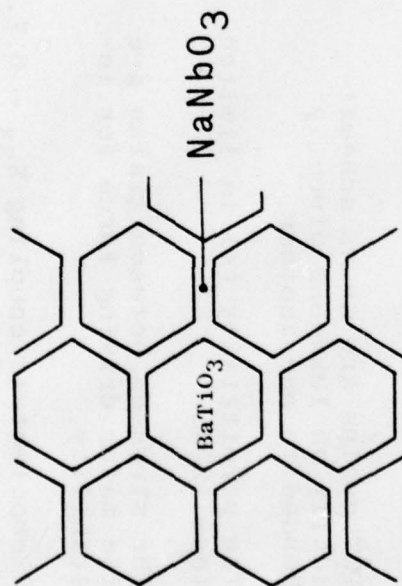
Proposed Composites



1. The grains are separated and bonded directly by a second ceramic phase.
2. Permittivity may be extended to $\sim 5,000$. Control nonlinearity and electroelastic aging by antiferroelectric phase which limits charge transfer necessary to domain motion.
3. Controls aging by controlling internal stresses through elastic properties of second phase.
4. Coupling $K_{33} \sim .7-.8$.
5. Mechanical strength comparable to current materials.

Fig. 2. Comparison of current material PZT to proposed new composites.

COMPOSITE DIELECTRICS



BaTiO_3 Grains
 NaNbO_3 2nd Phase

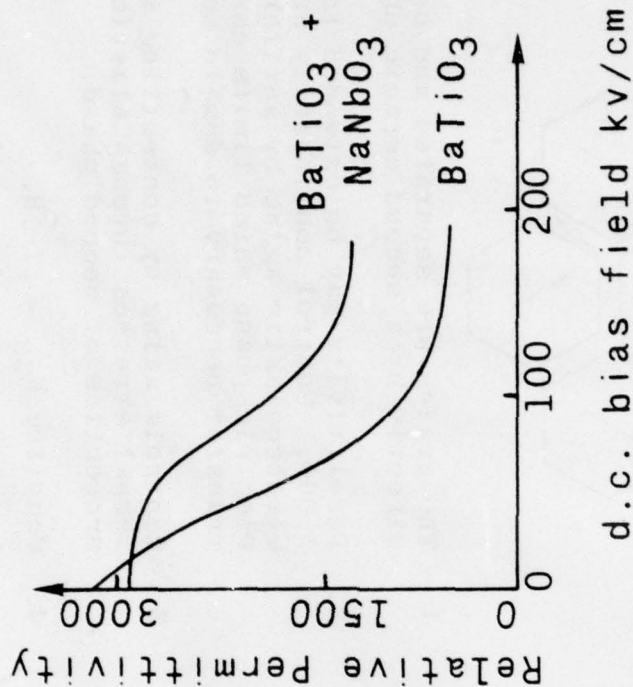


Fig. 3. Comparison of the dielectric properties of BaTiO_3 and a $\text{BaTiO}_3 + \text{NaNbO}_3$ composite. Note lower saturation of the permittivity in the composite as the bias field is increased.

along the grain boundaries significantly limits the loss of permittivity at higher voltages making a much more useful device. Further the NaNbO_3 actually aids the processing of such devices.

A second microstructural approach to the development of high permittivity materials would utilize the grain boundary phase to apply stress to the grains and hence raise the dielectric constant. The stress can be achieved by selecting a boundary phase with the appropriate thermal expansion difference from the grain phase. Such stresses must be kept within bonds to avoid spontaneous fracture of the grains. The thermal expansion differences, elastic properties, and especially the size of the grains and the thickness of the grain boundary phase are important parameters necessary to control the stress. Proper selection of elastic moduli of the two phases can be used to control the dependence of properties on other stresses such as poling. Alternately or in addition to such stress effects use of an antiferroelectric grain boundary phase may allow control of grain boundary charge and thus limit domain motion. This in turn should control losses and nonlinearities as discussed above.

Incorporating additional polarization mechanisms to the material that enhance permittivity is another approach to the development of higher (ϵ) materials. For example, the ceramic transducer could be processed in layers, e.g. by thick film techniques, with chemical differences in each layer. The chemical difference between layers should result in an additional polarization in the material.² This polarization would enhance poling, permittivity and could limit aging.

In addition to the above permittivity enhancing effects, other mechanisms such as non lossy domain wall motion should be explored. In summary there are a number of new opportunities to develop new high permittivity ceramic-ceramic composite materials for transducers that should be studied.

C. Electrostrictive Applications

A closely related opportunity to the development of high permittivity composite materials is to develop pure electrostrictive transducers that could be used in 'tuneable' arrays and special high power applications. Present transducers are 'poleable' ferroelectric materials. The polarization in these materials is permanent. Polarization, however, can be achieved by application of d.c. electric fields analogous to the use of magnetic fields with magnetostrictive materials. Strain is developed through electrostrictive behavior in these materials and is proportional to the square of the polarization which is proportional to the square of the applied

electric field and permittivity. Maximum strains, by pure electrostriction, of $10,000 \times 10^{-6}$ for BaTiO₃ and $60,000 \times 10^{-6}$ for PbTiO₃ are possible at room temperature. Strains, as large as 500×10^{-6} have been measured in BaTiO₃ + NaNbO₃ materials in preliminary Penn State University studies. Further, limited NRL work resulted electrostrictive materials consisting of BaTiO₃, alkali fluorides, and MgO having permittivities as high as 20,000, yet sinterable at temperatures up to 500°C lower than conventional BaTiO₃. These materials should have large electrostrictive effects and because of low sintering temperatures offer for the first time the possibility of using non noble electrodes in the multilayer devices discussed above.

Theoretically these electrostrictive materials have strains that can be as much as ten times larger than the supermagnetostrictive materials at room temperature. In addition electrostriction would utilize only voltage bias the magnitude of which could be controlled by permittivity and electrode separation. The technology of the capacitor industry offers the possibility of fabricating multi-electrode elements with small distances between electrodes. These elements could be used in electrostrictive applications with low voltage bias, e.g. ~ 100 volts which eliminates the need for large power supplies now needed by the supermagnetostrictive materials and uses a simpler technology. High ϵ materials thus offer the possibility of new large strain devices, e.g. high power at low electric fields.

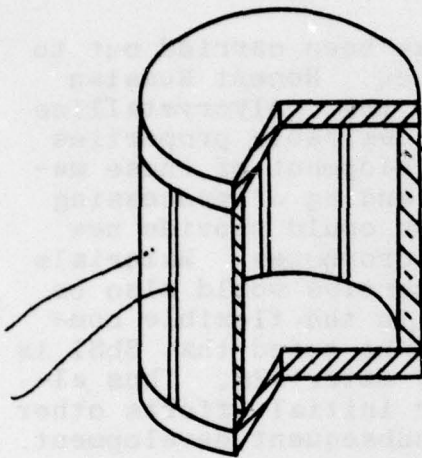
Therefore, electrostriction studies offer the possibility of developing high permittivity materials which can be fabricated at low temperatures permitting use of non noble electrodes. These materials offer the possibility of large strain devices.

D. New Compounds

Only a limited number of ternary compounds, mainly oxides, for sonar applications have been explored. This constitutes only a small fraction of the potential compounds of such usage, indicating a very large opportunity for future development. Clearly most of such development must be of a long term nature. However, there are also some important nearer term opportunities for developing hydrophone materials operating in a simple hydrostatic mode.

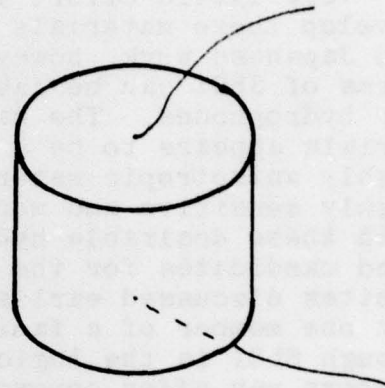
Current hydrophone systems use thin walled stacked PZT cylinders and achieve sensitivity by using striped electrodes (usually eight per cylinder) Fig. 4. The large number of leads and cylinders causes difficulties in manufacture and reliability problems in service. The development of materials

RELIABILITY



**Current Ceramic
PZT Cylinders**

1. Acoustic Amplifier
2. Thin ceramic shape difficult to manufacture & prone to handling fracture.
3. Multiple leads - give more reliability problems.



SbSI Type

1. Solid cylinder - easier to manufacture & less prone to fracture.
2. Two leads-greater reliability.

Fig. 4. Comparison of current materials to new materials shapes for hydrophone applications.

with large hydrostatic sensitivity would allow for a simpler design which would be more reliable. Highly anisotropic materials such as SbSI offer the possibility of up to ten times improvement in the hydrostatic coefficients Fig. 5, which makes feasible the simplified designs of Fig. 4.

Very little effort in the U.S. has been carried out to develop these materials for hydrophones. Recent Russian and Japanese work, however, indicates that polycrystalline forms of SbSI can be fabricated with desirable properties for hydrophones. The key to full development of these materials appears to be a basic understanding of processing highly anisotropic materials. Success could provide new highly sensitive and more reliable hydrophones. Materials with these desirable hydrostatic properties would also be good candidates for the active phase in the flexible composites discussed earlier. It should be noted that SbSI is but one member of a family of similar materials. Thus although SbSI is the logical choice for initial efforts other members may offer opportunities for subsequent development.

E. Microstructural Engineered Hydrostatic Materials

Closely related to the development of new hydrostatic compounds would be a study to engineer the desired hydrostatic sensitivity into composite materials by modifying the microstructure. Hydrostatic materials of this type could be used in the same applications as discussed above Fig. 4. One approach would be to reduce the interaction between the longitudinal and transverse piezoelectric coefficients. Further, other interactions such as changes in the signs of the piezoelectric coefficients should also be studied. Both theoretical analysis and experimental studies would be required to explore these possibilities.

F. Ferroelectric Glasses

Ferroelectric glasses should be perfectly poleable in any orientation and should have highly non-linear dielectric and optical properties because the polarizability cannot depend upon direction in glasses. Such glasses would be good candidates for optical hydrophones, dielectric amplifiers and possibly piezoelectric hydrophones. Further the range of possible properties of these glasses should offer a wide range of opportunities for new device development.

The existence of ferroelectric glasses was not anticipated by many. However, the possible existence of such glasses has now been demonstrated at Bell Telephone Laboratories.³⁻⁶ This has lead to study of the source or mechanism of such

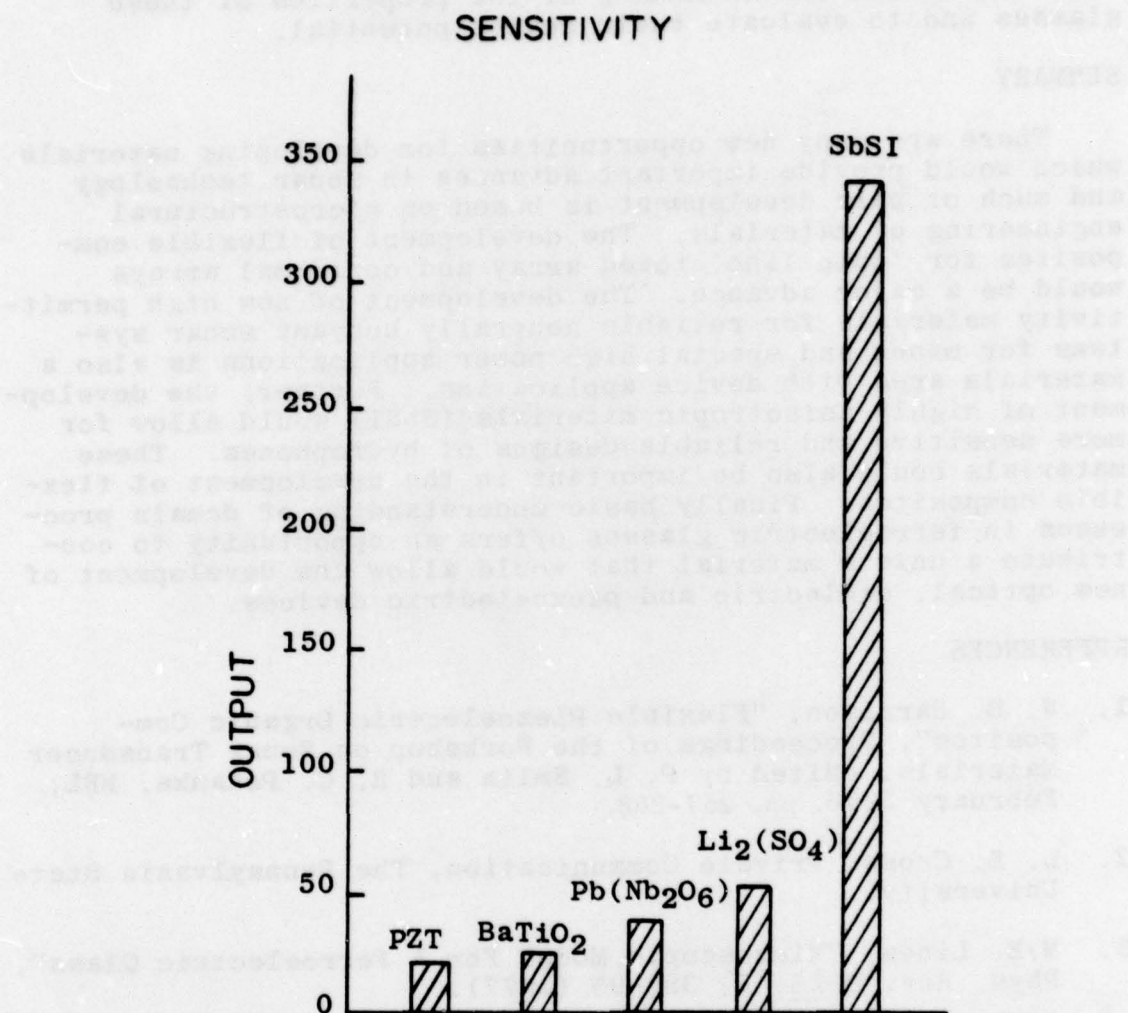


Fig. 5. Hydrophone sensitivity of piezoelectric materials in solid cylinder form.

ferroelectricity. Analysis at NRL shows that ferroelectric domains can exist in these materials. Additional experimental and theoretical work is necessary to develop both the fundamental understanding of the properties of these glasses and to evaluate their device potential.

SUMMARY

There are many new opportunities for developing materials which would provide important advances in sonar technology and much of this development is based on microstructural engineering of materials. The development of flexible composites for 'thin line' towed array and conformal arrays would be a major advance. The development of new high permittivity materials for reliable neutrally buoyant sonar systems for mines and special high power applications is also a materials area with device application. Further, the development of highly anisotropic materials (SbSI) would allow for more sensitive and reliable designs of hydrophones. These materials could also be important in the development of flexible composites. Finally basic understanding of domain processes in ferroelectric glasses offers an opportunity to contribute a unique material that would allow the development of new optical, dielectric and piezoelectric devices.

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Appendix A

Analysis of Composite Materials for Piezoelectric Applications

As a first step in evaluating composite structures two limiting cases were considered Fig. 1a. In Fig. 1a the two phases are stacked in series and 1b parallel. Since in Fig. 1a the electrical potential function must be continuous through both phases the model can be reduced to a simple two component stack Fig. 2a. Also if cross coupling between regions of the ceramic and polymer are neglected the parallel model can be simplified as shown in Fig. 2b. For the series model the applied stress must be continuous throughout both phases, and this stress through the piezoelectric coefficients (d) gives rise to the following charge in each element

$$Q(\text{ceramic}) = F d_c, Q(\text{polymer}) = F d_p \quad (1)$$

where Q = the charge developed (coulombs), F = applied force in newtons, and d = the piezoelectric coefficient coulombs/newton. Since the voltage (U) across each element must add to the total voltage

$$U_t = U_c + U_p = \frac{Q^*}{C^*} = \frac{Q_c}{C_c} + \frac{Q_p}{C_p} \quad (2)$$

where Q^* is the effective charge and C^* the effective capacitance of the composite, Q_c and Q_p the charge on each element, and C_c and C_p the capacitance of each element. From Eq. 2

$$d_{33}^* = \left(\frac{d_c}{C_c} + \frac{d_p}{C_p} \right) C^* \quad (3)$$

where

$$C^* = \frac{C_c C_p}{C_p + C_c} \quad (4)$$

Solving Eqs. 3 and 4 yields

$$d_{33}^* = \frac{C_c d_p + C_p d_c}{C_c + C_p} \quad (5)$$

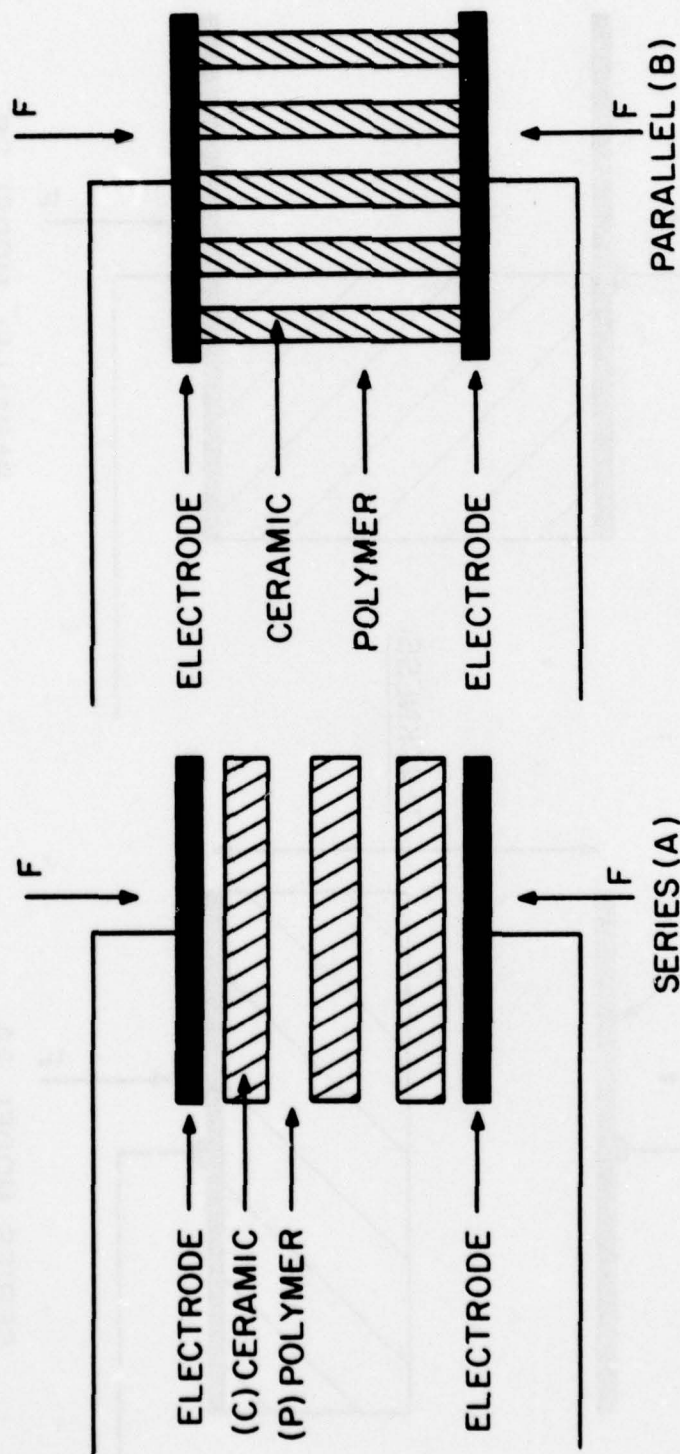


Fig. 1. Series and parallel combinations of composites.

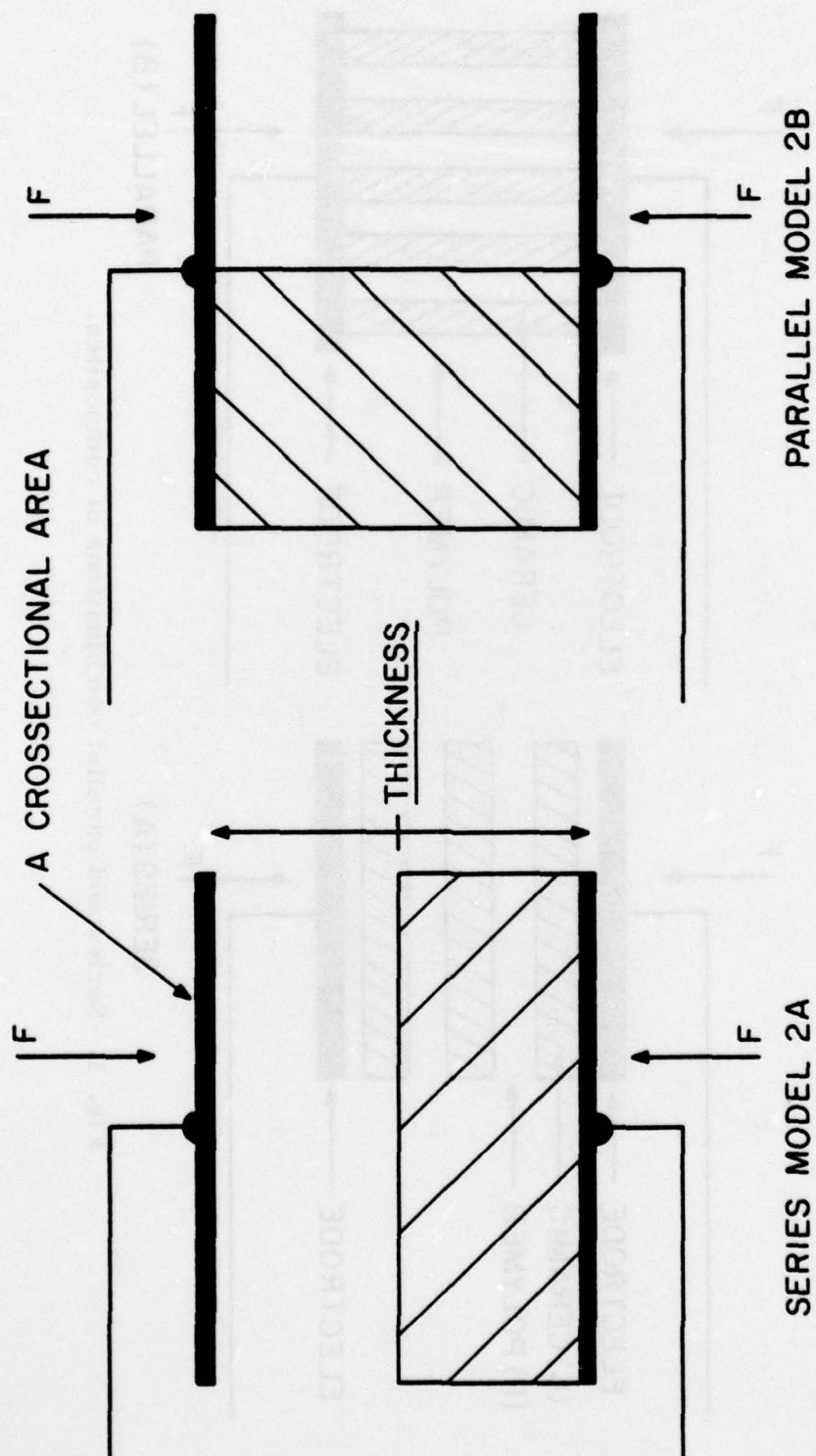


Fig. 2. Simplified series and parallel composites.

Since in general capacitance is related to permittivity through

$$C = \frac{\epsilon \epsilon_o A_i}{T_i} \quad (6)$$

and volume $V_i = A_i T_i$ to the crosssectional area and thickness Eq. 5 can be reduced to:

$$d_{33}^* = \frac{V_c d_c \epsilon_p + V_p d_p \epsilon_c}{V_p \epsilon_c + V_c \epsilon_p} \quad (7)$$

For the limiting case when d_p (polymer) = 0, $\epsilon_c \sim 1000 \gg \epsilon_p$ and the volume of polymer $\sim .1$ of the total volume Eq. 7 reduces to $d_{33}^* \sim d_c/100$ i.e. the charge coefficient must be significantly decreased in this type of structure. Further, since $\epsilon_{33}^* \sim 10 \epsilon_p$, $g_{33}^* = d_{33}^*/\epsilon \sim g_c$. Thus the voltage coefficient (g) will not be degraded from the ceramic value.

Thus for a series composite such as grains of ceramic embedded into a polymer matrix the dielectric and piezoelectric (d, charge) properties will be low. Further the piezoelectric voltage (g) will at best be that of the ceramic. Since a figure of merit for a hydrophone depends upon the product $g^2 \times \epsilon$ the series structure does not offer any possible improvement in properties over the ceramic alone.

For the parallel structure Figs. 1B, 2B the applied stress must be distributed throughout the structure as

$$F_t = F_c + F_p = \frac{1}{S_c} A_c N_c + \frac{1}{S_p} A_p N_p \quad (8)$$

with F_i = force, S_i is the reciprocal of the elastic modulus, A_c the crosssectional area, and N_i the strain. The charge developed by the parallel structure will be given by

$$Q_t = Q_c + Q_p \quad (9)$$

$$d_{33}^* F_t = d_c F_c + d_p F_p \quad (10)$$

Solving Eqs. 8, 9, and 10 simultaneously yields

$$d_{33}^* = \frac{d_c \frac{N_c A_c}{S_c} + d_p \frac{N_p A_p}{S_p}}{\frac{N_c A_c}{S_c} + \frac{N_p A_p}{S_p}} \quad (11)$$

For equal strain in each phase $N_p = N_c$ and since $A_i = V_i/T_i$ Eq. 11 can be reduced to:

$$d_{33}^* = \frac{d_c \frac{V_c S_p}{V_c S_p + V_p S_c} + d_p \frac{V_p S_c}{V_c S_p + V_p S_c}}{\frac{V_c S_p}{V_c S_p + V_p S_c} + \frac{V_p S_c}{V_c S_p + V_p S_c}} \quad (12)$$

Thus for a composite where $S_c \ll S_p$, $d_p = 0$, and $V_p \ll V_c$

$$d_{33}^* \sim d_c \quad (13)$$

and since

$$\epsilon_{33}^* = \left[\left(\frac{A_c}{T_c} \right) \epsilon_c + \left(\frac{A_p}{T_p} \right) \epsilon_p \right] \frac{T_t}{A_t} \quad (14)$$

ϵ_{33}^* can be adjusted between ϵ_c and ϵ_p by the amount of ceramic used. Since

$$g_{33}^* \sim \frac{d_c}{\epsilon_{33}^*} \quad (15)$$

g_{33}^* can be significantly increased by tailoring ϵ_{33}^* provided the applied stress is concentrated into the ceramic. Again since the figure of merit is $g^2 \times \epsilon$ the parallel structure offers the possibility of making improvements in flexible piezoelectric properties for hydrophone applications. Both of the above models (series and parallel) agree with an independent development at Pennsylvania State University.²

Preliminary experimental work has verified the general concepts of the parallel model. Fully polarized millimeter sized disks of lead zirconate titanate were incorporated into a silicone rubber matrix and the composite placed between two metal electrodes. The composite piezoelectric voltage coefficient was 750×10^{-3} volts/newton which is five times better than PVF₂ the leading flexible piezoelectric polymer material and 30 times that of the PZT ceramic alone.

REFERENCES

1. W. D. Kingery, Introduction to Ceramics, pp 719-731, J. Wiley, New York, 1967.
2. L. E. Cross, Private Communication, Pennsylvania State University.